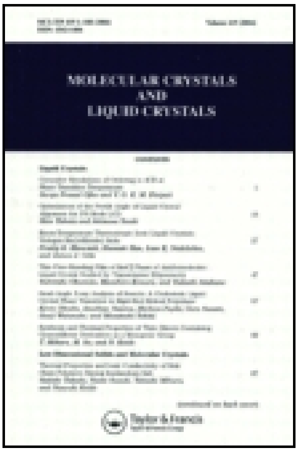

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Growth and Characterization of High T. Superconductor Single Crystals

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GROWTH AND CHARACTERIZATION OF HIGH Tc SUPERCONDUCTOR SINGLE CRYSTALS

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Abstract Single crystals of oxide superconductor ($ErBa_2Cu_3O_{7-\delta}$) were grown from a liquid phase using an excess CuO + BaO as a flux. The crystals were square thin plates (3 x 3 x 0.1mm^3) with large (001) faces on which various kinds of growth layers were developed including growth spirals. There was a certain correlation between Tc and the twinning. The measurements of Tc showed a large scatter in the value of Tc ranging from 65 to 90 K, in spite of a prolonged annealing and slow cooling in air or oxygen atmosphere. However, we found out for the first time a method to improve Tc by treating the solidified ingot in molten CrO_3. It turned out that the value of Tc before this treatment was improved to the extent of 85 to 92 K.

INTRODUCTION

Since the discovery in the La-Ba-Cu-O system of Tc~30K superconductors by Bednorz and Müller[1,2], many papers have been published on other series of oxide compounds with Tc~90K and 110K. Most of the specimens so far provided for investigations were polycrystals prepared by sintering the oxide powders[3-5]. It is necessary, however, to prepare high quality single crystals of those compounds in order to make clear their superconducting properties. The high quality single crystals will be successfully grown only with a correct knowledge of the growth mechanism.

The purpose of this experiment is to study the growth of single crystals of $ErBa_2Cu_3O_{7-\delta}$ and to improve their electrical property at low temperatures using a new heat-treatment. The $ErBa_2Cu_3O_{7-\delta}$ compound has been chosen as the most suitable material to grow the single crystals of 1-2-3 phase from the preliminary experiments.

EXPERIMENTAL

$ErBa_2Cu_3O_{7-\delta}$ single crystals were grown from a CuO excess solution at high temperature using a slow cooling method. The growth furnace used in this experiment has been described in the previous paper[6]. Typical heat-treatments are shown schematically in Figure 1, i.e. pre-sintered $ErBa_2Cu_3O_{7-\delta}$ + 3CuO were melted and cooled slowly at a rate of 6°C/h (Stage I). Platy $ErBa_2Cu_3O_{7-\delta}$ single crystals were grown in the solidified mass. Then the solidified mass was cut mechanically into several pieces, about half of them were kept in the as-cut state and the rest were coated thickly with molten CrO_3. They were put into an alumina crucible with a cover, heat treated at 900°C for 24h in air and cooled at a rate of 1°C/min (Stage II).

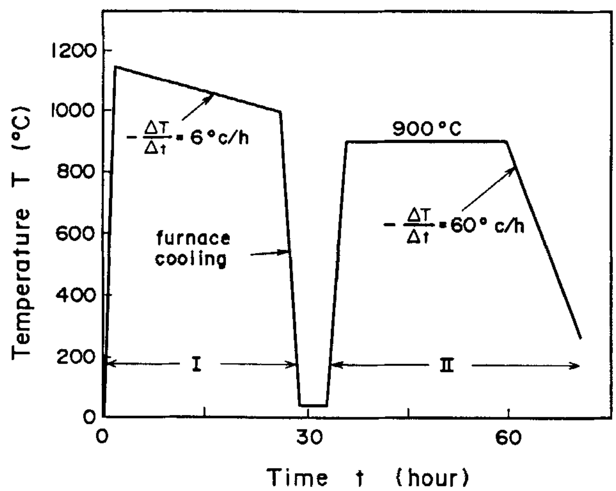

FIGURE 1 Heat-treatment to grow single crystals from the solution (Stage I) and to oxidize these crystals (Stage II).

Through this process the low temperature parts in the solidified mass were somewhat removed and porous parts remained containing many single crystals, which had been oxidized at various temperatures.

$ErBa_2Cu_3O_{7-\delta}$ single crystals were picked out by crushing these pieces, they were in the shape of plates with well-developed c-planes. The size of crystals normally obtained was about 3 x 3 x 0.1 mm^3.

EXPERIMENTAL RESULTS AND DISCUSSION

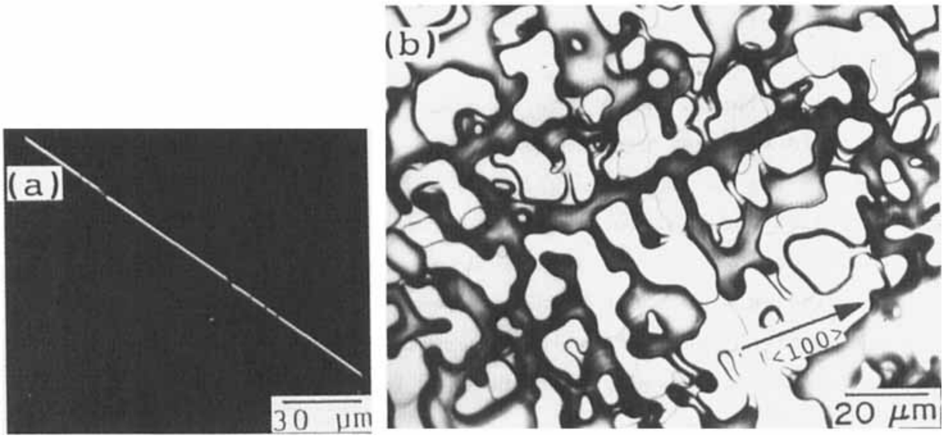

FIGURE 2 Typical morphologies of single crystals.
(a) A cross-section of the crystals.
(b) A c-plane with square growth layers and deep grooves.

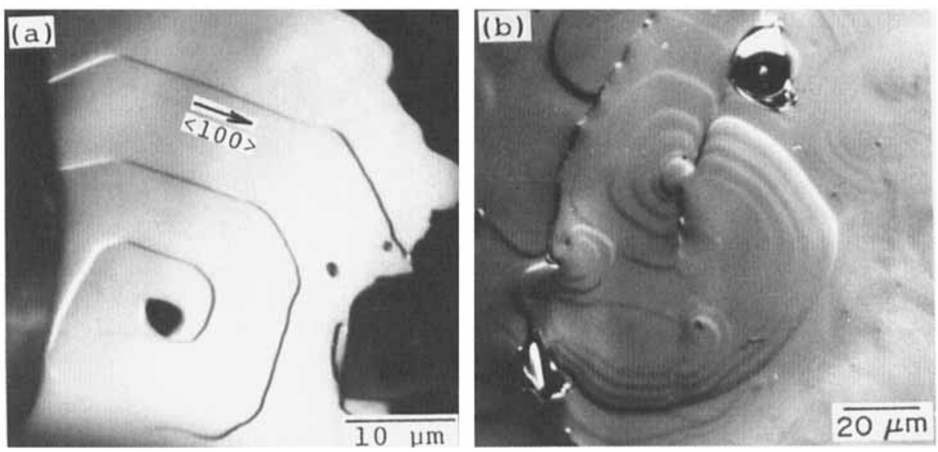

FIGURE 3 Step structures on the c-plane.
(a) A spiral pattern.
(b) Step loops from pair screw dislocations at a sub-boundary.

The observations on the surfaces of single crystals were carried out in detail using a differential interference microscope. A typical morphology of a cross section and a c-plane of a single crystal are shown in Figure 2. The thickness of crystals obtained was a range from about 10 to 200 μm. As is seen from Figure 2(b), the surface structure was characterized by a number of square layers with high steps and deep grooves running parallel to the direction of <100>.

Spiral patterns, which were induced by screw dislocations with large Burgers vectors, were frequently observed on the broad terrace (Figure 3(a)). The straight step segments of the spiral pattern were also parallel to the <100> direction due to a crystallographic anisotropy. Figure 3(b) shows an example of half step loops originated from a sub-boundary where pair screw dislocaions were presumably formed. From the observation results, single crystal surfaces are composed of various step structures leading to a layer growth mechanism.

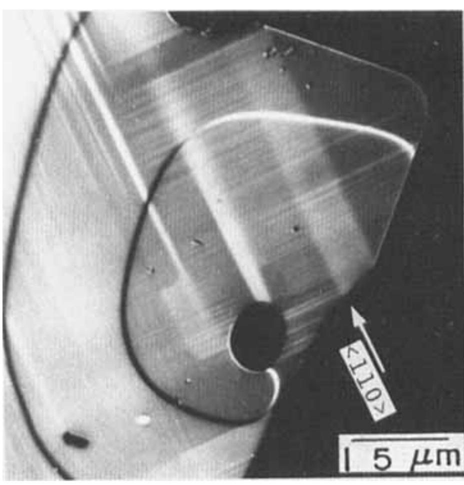

FIGURE 4
Twin striations along the <110> direction.

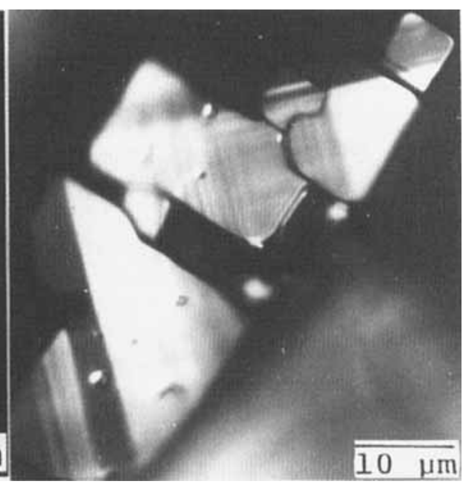

FIGURE 5
A single crystal united with several small crystals.

Figure 4 shows fine striations due to twinning introduced by the phase transition from tetragonal to orthorhombic structure, running parallel to the direction of <110>. These striations are useful to determine the crystallographic direction in small area of a crystal. Figure 5 shows juxtaposition of small platy crystals. It is judged from the striations of twinning that they were united by adjusting the mutual direction to each other in the earlier growth stage. This kind of juxtaposition is dominantly observed in the present crystals.

In general, platy single crystals obtained in the as-grown state do not show a high quality of superconductivity[7,8]. This is perhaps due to a large amount of oxygen deficiencies in the crystals grown under a reducing circumstance at higher temperature. So, a proper heat-treatment is required to supply the oxygen atoms to the crystals. For single crystal specimens heat treated by three different techniques: (a) furnace cooling only with solidified mass in air, (b) slow cooling with solidified mass in air and (c) slow cooling with solidified mass coated with CrO_3, measurements of electrical resistivity were performed at low temperatures above 65K, and then the values of transition temperature Tc (midpoint) and transition width ΔTc were compared. Figure 6 is a summary of Tc for many specimens heat treated by three different techniques of (a), (b) and (c). In the cases (a) and (b), the scatters of Tc are in a broad range and that indicate for the oxygen deficiencies not to be occupied enough. In the last case (c), Tc-values for all of the specimens gathered around 90K. It seems that oxygen atoms emitted by decomposition of CrO_3 at high temperature, transferred to the solidified mass and then absorbed by the single crystals imbedded in the solidified mass. The representative curve of the resistivity is presented in Figure 7, where it showed a metallic behavior above Tc and dropped to the zero-value at 91K.

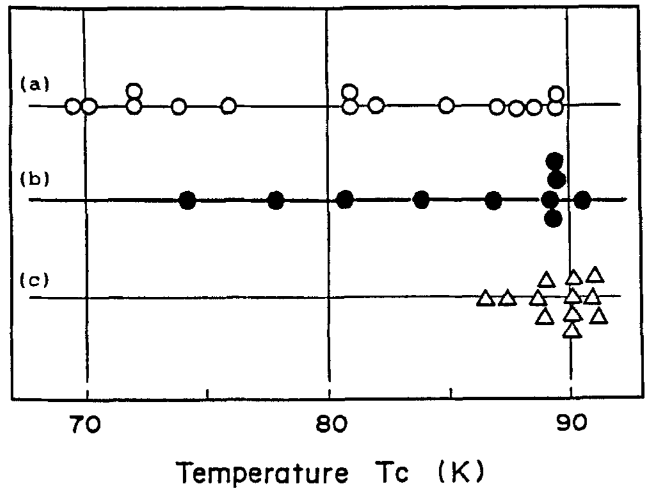

FIGURE 6 Distribution of Tc:
(a) for the specimens heat treated by furnace cooling only with solidified mass.
(b) for the specimens heat treated at the cooling rate of 60°C/h with solidified mass in air.
(c) for the specimens heat treated at the cooling rate of 60°C/h with solidified mass coated with CrO_3.

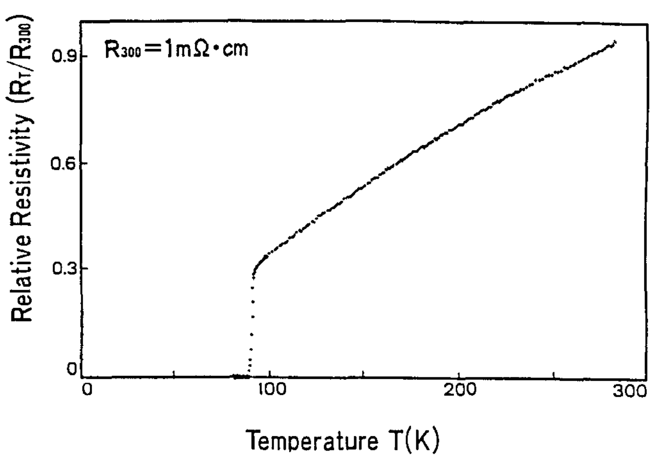

FIGURE 7 Temperature dependence of the relative resistivity (R_T/R_{300}). The specimen was heat treated with solidified mass coated with CrO_3.

SUMMARY

Summarizing the experimental results with regard to the growth and heat-treatment for $ErBa_2Cu_3O_{7-\delta}$ single crystals, we note the following:

(1) Platy single crystals were grown from a CuO excess solution using a slow cooling method.

(2) The crystals were in the shape of a plate with well-developed c-planes and were of about 3 x 3 x 0.1 mm^3 in size. Various kinds of growth layers with high steps were observed on these planes, leading to a layer growth mechanism. Juxtaposition of small platy crystals were observed in an early growth stage, in which crystals were united by adjusting the mutual direction to each other.

(3) When these single crystals were heat treated with CrO_3 coating, they showed high quality superconductivity of Tc~90K (ΔTc~3K).

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